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MONOVALENT EUROPIUM IN NaCl–Eu AND KCl–Eu

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As is known, for all lanthanides the trivalent state is typical in chemical compounds and phosphors. In a number of cases divalent ions may also arise, primarily those of europium, samarium, and ytterbium; recently it has also proved possible to reduce impurity ions Pr, Nd, Dy, Er, Ho, and Tu to the divalent state in MeF_2. (A review of work on these questions is contained in (^{1}).)

The possibility of the occurrence of monovalent impurity centers of rare-earth elements was first discussed by N. A. Gorbacheva (^{2}) (using europium in strontium-magnesium orthophosphate as an example). Later Fong and Käzig (^{3}) found in a KCl–Sm crystal a monovalent state not typical of rare-earth elements: Sm^{2+} ions were reduced to Sm^+ under x-ray irradiation.

Below we describe the conditions for the formation and luminescence of Eu^+ ions in NaCl and KCl crystals.

The correlation between photoluminescence bands and EPR spectra of NaCl–Eu and KCl–Eu single crystals was studied (grown in sealed ampoules; Eu content 0.1 mole % in the melt).

In the available works on luminescence of NaCl–Eu (^{4}, ^{5}), an intense band is indicated in the emission spectrum with $\lambda_{\max} = 425$ mμ, associated with electronic transitions in Eu^{2+}: $4f^7(^8S_{7/2}) \rightleftarrows 4f^6 5d$. In (^{5}) it is also shown that after high-temperature annealing and slow cooling of the crystal, a second band appears in its luminescence with $\lambda_{\max} = 455$ mμ, which disappears after quenching the crystal by rapid cooling from 350°C.

We have established that in NaCl–Eu crystals quenched from 650°C, two emission bands are excited by ultraviolet light: at 425 and 455 mμ (Fig. 1a). Decomposition of the unstable solid solution NaCl–Eu (during prolonged storage or slow cooling of annealed crystals) leads to destruction of the 425 mμ band and the simultaneous appearance of a new, low-temperature emission band with $\lambda_{\max} = 407$ mμ, and to strengthening of the 455 mμ band (Fig. 1b).

Fig. 1. Luminescence spectra of NaCl—Eu crystals

Figure 1: Fig. 1. Luminescence spectra of NaCl—Eu crystals

In NaCl—Eu, at a frequency of 9.4 GHz, an EPR spectrum of Eu^{2+} ions is observed, consisting of 14 groups of fine-structure lines. Each group consists of two sextets of hyperfine structure from the isotopes Eu^{151} and Eu^{153}, characterized by the hyperfine-splitting constants: $A(\mathrm{Eu}^{151}) = 34 \pm 1$ Oe; $A(\mathrm{Eu}^{153}) = 15.1 \pm 0.3$ Oe. From the fine-structure spectra it is evident that two inequivalent Eu^{2+} centers are present: with rhombic and tetragonal symmetry in the NaCl lattice in the ratio $\sim 10 : 1$*. Studies ([6], [7]) on the EPR of NaCl—Eu crystals showed that at room temperature and below, the principal part of the Eu^{2+} impurity isomorphously substitutes for Na^+ and is associated with a cation vacancy V^+. When the temperature is raised to 300°C, however, the overwhelming majority of such centers dissociate, becoming Eu^{2+} centers with cubic symmetry ([7]). However, as follows from ([4]), no shift of the maximum of the 425 mμ band is observed in this case.

* Tetragonal centers are observed in powders, where rhombic centers are not visible.

Since we observe a correlation of the intensity of the EPR lines (in quenched and unquenched crystals) with the intensity of the main luminescence band at 425 mμ, it is logical to assign the latter to luminescence of centers ($\mathrm{Eu}^{2+}V^+$) at lattice sites. At the same time, some fraction

Fig. 1. Luminescence spectra of NaCl—Eu crystals: **a** —one day after quenching; **b** —annealed; **c** —additively colored with quenching (1), with annealing (2); **d** —X-irradiated for 30 min at 300°K, quenched (1), annealed (2), 15 min after X-irradiation (3). All curves were recorded at 77°K, except for the dotted curves in **a**, **b** (300°K). Intensity is plotted in arbitrary, but everywhere identical, units.

Eu^{2+}, possibly, is arranged in the crystals in another manner, which is manifested in the presence of a luminescence band with $\lambda_{\max} = 455$ mμ.

During the decomposition of the unstable solid solution NaCl—Eu, part of the impurity segregates in the form of microinclusions of the $EuCl_2$ phase, which give in the crystal a low-temperature luminescence band with $\lambda_{\max} = 407$ mμ.* At high temperatures the microphase "dissolves." Rapid cooling fixes this state, and in freshly quenched crystals there is therefore only one kind of Eu^{2+} luminescence at lattice sites (425 mμ).

Additive coloring of NaCl—Eu in sodium vapor (with subsequent rapid cooling) leads to a sharp decrease of the luminescence band at 425 mμ and to the appearance of a new band at 480-500 mμ (Fig. 1c). The same occurs in crystals that were slowly cooled after coloring,** but in them the luminescence of the $EuCl_2$ microphase is also manifested,

* Photoluminescence of the microphase at low temperatures is also characteristic

of other unstable solid solutions, for example NaCl—Cu or Na(Cl, I)—Ag (8).

** In this process the F-bands ($\lambda_{\max} = 455$ mμ) are destroyed (9). In quenched crystals, however, luminescence with $\lambda_{\max} = 480$ mμ remains because of reabsorption by F-centers.

which, consequently, does not localize electrons. The creation in the crystal of quasi-free holes and electrons during X-irradiation suppresses the microphase luminescence band (Fig. 1e), which indicates capture of holes on it with probable ionization of Eu^{2+} to the trivalent state.

X-irradiation also leads to destruction of the 425 mμ band and the appearance of a new, broad luminescence band at 480–500 mμ (Fig. 1e, g, curves 1, 2). At room temperature in irradiated crystals the initial state is rapidly restored owing to recombination of electrons and holes (Fig. 1g, curve 3). Both in additively colored and in X-irradiated crystals the intensity of the EPR spectrum of Eu^{2+} ions at sites of the NaCl lattice decreases sharply. The parallel destruction in these cases of the 425 mμ band, owing to the emergence of the 480–500 mμ band, indicates capture by Eu^{2+} centers of quasi-free electrons. In this process europium passes into the monovalent state. The spectroscopy of free Eu^+ ions has been well studied. Its outer shells are: $4f^7 5s^2 5p^6 6s^1$. The most probable transitions are $4f^7 6s$ $(^7S^9_3 S_4) \rightleftarrows 4f^7 6p$ $(^7P^9_{2,3,4} P_{3,4,5})$, corresponding to emission lines in the region from 350 to 450 mμ (10). Naturally, the observed luminescence of Eu^+ in NaCl in the region 480–500 mμ should be correlated with the indicated electronic transitions. The "blurring" of the band and its shift to longer wavelengths occur because of strong compression of the energy levels of the impurity ions in the crystal lattice (11).*

It should be noted that in works (4,5) the transformation of europium impurity ions in alkali halides under the action of X-rays was also indicated; near 400 mμ, absorption bands of the activator "induced" by irradiation were found. Apparently, this absorption is due to Eu^+ ions.

KCl—Eu crystals give a single luminescence band at 415 mμ, which is associated with Eu^{2+} at sites of the KCl lattice; it does not change after annealing and quenching (a stable solid solution) (4,5). Additive coloration, as well as X-irradiation, sharply weakens this band. The EPR spectrum of Eu^{2+} ions in KCl is similar to the spectra from NaCl—Eu, and is characterized by hyperfine-splitting constants $A(\mathrm{Eu}^{151}) = 33.6 \pm 1$ Oe and $A(\mathrm{Eu}^{153}) = 14.9 \pm 0.5$ Oe. In all cases—annealing with slow cooling, quenching, additive coloration, X-irradiation—the intensity of the EPR spectrum changes in parallel with the luminescence intensity at the maximum at 415 mμ. After additive coloration of KCl—Eu, a weak new band appears in its luminescence spectrum in the region of 470 mμ. After X-irradiation it could not be observed. As in the case of NaCl—Eu, we suppose that part of the Eu^{2+} impurity captures electrons with formation of Eu^+ in the KCl lattice.

Thus europium is the only one of the known activators in which all three differently valent ions—Eu^+, Eu^{2+}, and Eu^{3+}—possess the ability to luminesce in crystals.

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* Ionic radii: $r(\mathrm{Eu}^0) = 2.02$ Å (according to Belov and Bokii), $r(\mathrm{Eu}^{2+}) = 1.24$ Å (according to Arens), $r(\mathrm{Eu}^{+})$, naturally, is close to $r(\mathrm{Eu}^0)$. The lattice parameter of NaCl is $a = 5.63$ Å; therefore "geometrically" Eu^+ can be accommodated only adjacent to a vacancy V^+.

Note: Figure translations are in progress. See original paper for figures.

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